FUNCTIONALIZED SILICAS

Introduction and Background

The present invention relates to functionalized silicas, a process for their preparation and their use.

It is known to react silicon dioxide obtained by flame hydrolysis and with a surface area of 40 to 200 m^2/g with 3-methacryloxypropyltrimethoxysilane. The resulting silicon dioxide is then coated with a further shell of (meth)acrylate polymers and subsequently employed in dental compositions (EP 0 142 784 A1).

Summary of the Invention

The present invention provides functionalized silicas, characterized by functional groups fixed on the surface, the groups being 3-methacryloxypropylsilyl and/or glycidyloxypropylsilyl.

The present invention also provides a process for the preparation of the functionalized silicas, which is characterized in that a silica is sprayed optionally first with water or dilute acid and then with a surface modification reagent or a mixture of several surface modification reagents in a suitable mixing vessel, with intensive mixing, the components are optionally re-mixed for 15 to 30 minutes and heat-treated at a temperature of 100 to 400 °C over a period of 1 to 6 h.

A silica prepared pyrogenically by the route of flame hydrolysis of $SiCl_4$ can preferably be employed as the silica. Such pyrogenic silicas are known from Ullmanns Enzyklopädie der technischen Chemie [Ullmanns Encyclopaedia of Industrial Chemistry], 4th edition, volume 21, page 464 (1982).

In a preferred embodiment of the invention, a pyrogenic silica with a surface area of approx. 200 m^2/g can be employed (Aerosil® 200).

Monomeric substances, such as 3-methacryloxypropyltrialkoxysilane and/or glycidyloxypropyltrialkoxysilane, wherein alkoxy can be methoxy, ethoxy and/or propoxy, can be employed as the surface modification reagent.

The amount of silane can be metered with respect to the silica such that no or only a small excess results. The excess silane can optionally be removed during the heat treatment.

The silica according to the invention can be employed in solvent-containing coatings, for example 2-component polyurethane coatings.

Detailed Description of Invention

The functionalized silicas according to the invention have the following advantages: When used in solvent-containing coatings, such as, 2-component polyurethane coatings, the scratch resistance of the coating surface is increased.

According to the invention, the pyrogenically prepared silicas according to table 1 can be employed as the silica for the silanization.

Table 1

Physico-chemical data of AEROSIL®

Test method		AEROSIL 90	AEROSIL 130	AEROSIL 150	AEROSIL 200	AEROSIL 300	AEROSIL 380	AEROSIL OX 50	AEROSIL TT 600
Behaviour towards water		hydrophilic							
Appearance		loose white powder							
BET surface area[1]	m2/g	90±15	130±25	150±15	200±25	300±30	380±30	50±15	200±50
Average primary particle size	nm	20	16	14	12	7	7	40	40
Tamped density approx. values[2]	g/l	80	50	50	50	50	50	130	60
Compacted goods (added "V")	g/l	120	120	120	120	120	120		
VV goods (added "VV")[12]	g/l g/l			50/75	50/75 120	50/75 120			
Loss on drying[3] (2 hours at 105 °C) on leaving supply works	%	<1.0	<1.5	<0.5[9]	<1.5	<1.5	<2.0	<1.5	<2.5
Loss on ignition[4] [7] (2 hours at 1000°C)	%	<1	<1	<1	<1	<2	<2.5	<1	<2.5
pH[5]		3.7-4.7	3.7-4.7	3.7-4.7	3.7-4.7	3.7-4.7	3.7-4.7	3.8-4.8	3.6-4.5
SiO_2[8]	%	>99.8	>99.8	>99.8	>99.8	>99.8	>99.8	>99.8	>99.8
Al_2O_3[8]	%	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.08	<0.05
Fe_2O_3[8]	%	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.01	<0.003
TiO_2[8]	%	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
HCl[9][10]	%	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Sieve residue[9] (Mocker method, 45 µm)	%	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.2	<0.05
Drum size (net)[11]	kg	10	10	10	10	10	10	10	10

1) in accordance with DIN 66131
2) in accordance with DIN ISO 787/XI, JIS K 5101/18 (not sieved)
3) in accordance with DIN ISO 787/II, ASTM D 280. JIS K 5101/21
4) in accordance with DIN 55921, ASTM D 1208, JIS K 5101/23
5) in accordance with DIN ISO 787/IX, ASTM D 1208, JIS K 5101/24
6) in accordance with DIN ISO 787/XVIII, JIS K 5101/20
7) based on the substance dried for 2 hours at 105 °C
8) based on the substance ignited for 2 hours at 1000 °C
9) special packaging protecting against moisture
10) HCl content is a constituent of the loss on ignition
11) V goods are supplied in sacks of 20 kg
12) VV goods are currently supplied only from the Rheinfelden works

Example 1:

Aerosil® 200 is mixed with 4 parts water and 18 parts 3-methacryloxypropyl-trimethoxysilane (for example DYNASILAN MEMO) and the mixture is heat-treated at 140 °C under an inert gas.

The silica obtained has the following properties:

BET [m^2/g]	138
Tamped density [g/l]	52
pH	4.6
C content	5.7
Loss on drying [%]	0.8
Loss on ignition [%]	9.7
DBP number [%]	228

Example 2:

Aerosil® 200 is mixed with 3 parts water and 16 parts 3-glycidyloxypropyl-trimethoxysilane (for example DYNASILAN GLYMO) and the mixture is heat-treated at 140 °C under an inert gas.

The silica obtained has the following properties:

BET [m^2/g]	165
Tamped density [g/l]	53
pH	4.9
C content	5.5
Loss on drying [%]	1.5
Loss on ignition [%]	8.7
DBP number [%]	242

Experiment 1:

A conventional 2-component polyurethane coating has been used to investigate the improvement in the scratch resistance. The recipe for the coating and the preparation, including the application, are summarized in the following:

Recipe:

		Parts by wt.
Millbase	Setalux C 1152, XX – 51.50 % (Akzo Nobel)	53.3
	Butyl acetate 98 %	6.7
	Xylene	6.7
	AEROSIL (silica according to example 1)	5.0
	Σ	**71.7**
Lacquer constituents:	Setalux C 1152, XX – 51.50 % (Akzo Nobel)	1.1
	Xylene	12.2
	Ethoxypropyl acetate	1.5
	Butylglycol acetate	1.5
Hardener:	Desmodur N 75 (Bayer)	17.0
	Σ	**105.0**

Binder concentration:	40 %
AEROSIL® calculated with respect to the millbase (SC):	18.8 %
AEROSIL® calculated with respect to the coating (total):	5 %

AEROSIL® calculated with respect to the coating (SC): 12,5 %

Preparation and application of the coatings

The Setalux is mixed with the solvents. For predispersion, the AEROSIL® is then incorporated into this mixture with a dissolver (disc ∅ 45 mm) and predispersed for 5 min at 2000 rpm. The mixture is dispersed in a laboratory bead mill for 30 min at 2500 rpm and a pump output of 60 % using glass beads (∅ approx. 1 mm). The dispersing quality is checked with a grindometer, 25 µm, in accordance with DIN ISO 1524. It must be smaller than 10 µm.

The lacquer constituents are added to the millbase in accordance with the recipe, the components being mixed with a blade stirrer at 2000 rpm. The hardener is stirred into the mixture in the same manner.

After the coatings have been adjusted to the spray viscosity according to DIN 53411, the coatings are applied to black-lacquered metal sheets, for example DT 36 (Q-Panel), by means of spraying application (layer thickness about 40-50 µm). After the spraying, the metal sheets are dried for 24 h at room temperature and then for 2 h in a drying oven at 70 °C.

Scratching experiments:

The metal sheets are scoured with a quartz/water slurry (100 g water + 1 g Marlon A 350, 0.25 % + 5 g Millicarb BG) with the aid of a scouring and washing resistance testing machine (Erichsen, brush with pig bristles). The shine before and 10 min after scouring is determined with a reflectometer (20 ° incident angle).

Table 2

Summary of the coating-relevant properties of the liquid coatings and of the films applied and dried:

		AEROSIL 200	Silica/ (example 1)	Reference
Grindometer value	**[µm]**	<10	<10	-
Viscosity (millbase)	**[mPas]**			
	6 rpm		1000	180
	60 rpm	464	600	143
Viscosity (coating + hardener)	**[mPas]**			
	6 rpm	166	180	75
	60 rpm	141	147	62
Dilution (adjustment to 20 s DIN 4 mm)	**[%]**	11.5	8.5	1.7
Scratch resistance				
20 ° reflectometer value before scratching		90.9	87.6	91.3
40 strokes with Sikron F 500		66.4	73.0	50.7
20 ° reflectometer value residual shine		73.0	83.3	55.5
100 strokes with Millicarb BG 20 °		79.2	80.5	68.4
reflectometer value residual shine [%]		87.1	91.9	74.9

Further variations and modifications of the foregoing will be apparent to those skilled in the art and are intended to be encompassed by the claims appended hereto.

European priority application 00 122 954.1 is relied on and incorporated herein by reference.